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"FLEXIBLE" NEMATIC POLYMERS : STIFFENING NEAR THE CLEARING POINT

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Abstract Polymers composed of a nematogenic backbone plus a relatively long "spacer", are quite flexible in the isotropic fluid state. However, when the melt is cooled down towards the nematic transition point T_c, each monomer aligns the surrounding medium, and this induced alignment reacts on other monomers from the same chain. A simple (mean field) estimate of this effect gives a persistence length l_p increasing like the square of the nematic correlation length ξ. Thus, near T_c, the chains must be rigid. This may explain why "flexible" polymers show pretransitional properties which differ from those of the monomer, and are rather of the Onsager Flory type, together with a large jump of the order parameter at T_c.

INTRODUCTION

A certain number of nematic polymers of the "backbone" type have been studied recently[1] (figure 1). Even when the aliphatic "spacer" is long, it has been found that :

A) The order parameter S in the nematic melt is much higher (at the same reduced temperature T/T_c) for the polymer than for the monomer[2].

B) The magnetic birefringence-measured just above the clearing point T_c-has very specific features for the polymer[3] : as usual, the Cotton Mouton constant CM follows a law $(CM)^{-1} = \alpha(T-T^*)$ but both α and T_c-T^* are much higher for the polymer than for the monomer.

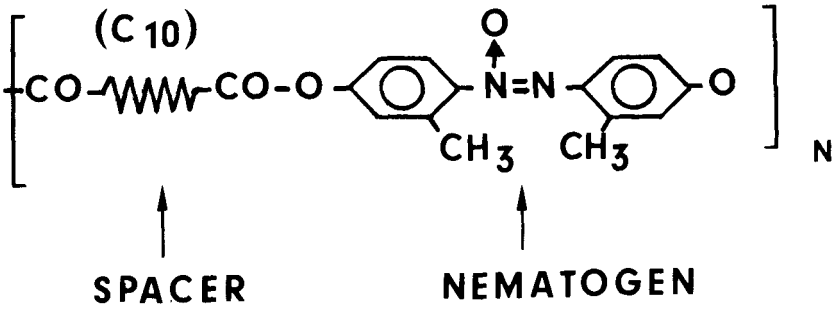

FIGURE 1. A typical "backbone" nematic polymer : "DDA9". The mesogenic part is related to PAA. The spacer is a C_{10} aliphatic chain, and is thus relatively long, allowing for flexibility.

This is a surprise : magnetic birefringence measurements on dilute solutions of the same polymer (DDA9) in conventional (isotropic) solvents, show that the chain is quite flexible : the persistence length l_p being at most 1.7 (monomer length). In the nematic phase of the pure polymer, we can easily understand that each chain is strongly aligned by the surrounding medium, and fluctuates only weakly from a stretched conformation[4-6]. But in the isotropic melts, well above the clearing point T_c, the magnetic birefringence data[1] show clearly that the DDA9 chains are just as flexible as in dilute solution : then we do not understand the differences between monomers and polymers as measured by magnetic birefringence just above T_c.

The aim of the present note is to present one possible line of explanation, based on monomer/monomer interactions for two relatively distant monomers of the same chain : the interaction being mediated by the surrounding chains. The analysis is very primitive, but it does suggest that the chains may become rather rigid inside a temperature interval $T-T_c \sim 10°K$ above the clearing point. This in turn gives a hint on the nature of the transition : for the monomer we expect, as usual, a nearly second order transition with a very small interval $T_c-T^* \sim 1°K$. But for the polymers, if they behave like rigid rods on the scale of the correlation length ξ, we expect a transition more related to what Onsager[7] and Flory[8] computed long ago, with a strong first. order character, and a larger interval T_c-T^*. Thus, our aim is to show that, near T_c, the persistence length l_p may become larger than the correlation length ξ (although ξ itself is getting large).

INDIRECT INTERACTIONS

Our starting point will be a wormlike model for one chain C, t being the length measured along the chain, $\underset{\sim}{r}(t)$ the corresponding monomer position, and $\underset{\sim}{u} = d\underset{\sim}{r}/dt$ a unit vector tangent to the chain. The alignment tensor for the chain is

$$S_{\alpha\beta}(t) = u_\alpha(t)\, u_\beta(t) - \frac{1}{3}\,\delta_{\alpha\beta} \tag{1}$$

We describe the other chains surrounding C, as a continuous medium with a tensor order parameter $Q_{\alpha\beta}(\underset{\sim}{r})$ dependent on the observation point $\underset{\sim}{r}$. We write the free energy of the chain plus its surroundings in the form $F = F_C + F_M$. F_C describes the couplings between chain and medium :

$$F_C = -\Lambda \int dt \int d\underset{\sim}{r}\; S_{\alpha\beta}(t)\; Q_{\alpha\beta}(\underset{\sim}{r})\; \delta\left[\underset{\sim}{r} - \underset{\sim}{r}(t)\right] \tag{2}$$

while F_M is the continuum energy in a Landau form[9]

$$F_M = \int d\underset{\sim}{r} \left[\frac{1}{2}\, A(T)\; Q_{\alpha\beta} + \frac{1}{2}\, L\; (\nabla Q_{\alpha\beta} \,.\, \nabla Q_{\alpha\beta})\right] \tag{3}$$

In Eqs. (2), (3), summation over repeated indices is assumed. The structure of the gradient terms in (3) has been outrageously simplified (we come back to this point in section "Persistence length"). Note that A and Λ are not entirely independent, since the energy contribution to A originates mostly from the coupling Λ. The nematic correlation length ξ is given by

$$\xi^2 = L/A(T) \tag{4}$$

For our purposes we shall not need to specify the temperature variations of A(T) in detail, but we recall that A becomes small, and ξ large, near the clearing point T_c.

Optimising the sum $F_C + F_M$ with respect to $Q_{\alpha\beta}$, and solving the resulting equation, we find

$$Q_{\alpha\beta}(\underset{\sim}{r}) = \frac{\Lambda}{4\pi L}\int dt\ S_{\alpha\beta}(t)\ \rho^{-1}\ \exp(-\rho/\xi) \qquad (5)$$

where $\rho = |\underset{\sim}{r}(t)-r|$.

The resulting contribution to the chain energy is

$$\delta F_C = -\frac{1}{2}\frac{\Lambda^2}{4\pi L}\int dt\ dt'\ S_{\alpha\beta}(t)\ S_{\alpha\beta}(t')\ \rho^{-1}\ \exp(-\rho/\xi) \qquad (6)$$

where $\rho(tt') \equiv |\underset{\sim}{r}(t) - \underset{\sim}{r}(t')|$. Eq. (6) defines the indirect interaction between chain units : it is a quadrupole/quadrupole coupling, and is slowly decreasing with the distance ρ, up to $\rho = \xi$. Note that the tensor product (SS) may be simplified :

$$S_{\alpha\beta}(t)\ S_{\alpha\beta}(t') \equiv (\underset{\sim}{u}(t).\underset{\sim}{u}(t'))^2 - \frac{1}{3} \qquad (7)$$

PERSISTENCE LENGTH

A general discussion of chain conformations with the coupling (6) would be extremely complex. Here, as we shall see, in the interesting range, the persistence length l_p will turn out to be often larger than ξ : this allows to take a nearly rigid chain as our starting point, i.e. to replace $\rho(tt')$ by $|t-t'|$.

Let us then compute the rigidity modulus B of the chain, due to the interactions (6). This is defined as follows : if the chain is bent, with a (large) radius of curvature R, the bonding energy (per unit length) is $B/2R^2$. To obtain B we consider the bent chain of Fig. 3, and sum the interaction energies from the point (t) to all neighboring points $(t+\tau,\ \tau>0)$. If ε is the angle between $\underset{\sim}{u}(t)$ and $\underset{\sim}{u}(t+\tau)$ we have $\varepsilon = \tau/R$ and $(\underset{\sim}{u}(0).\underset{\sim}{u}(\tau))^2 \cong 1 - \varepsilon^2 = 1 - \tau^2/R^2$.

Then the curvature energy is

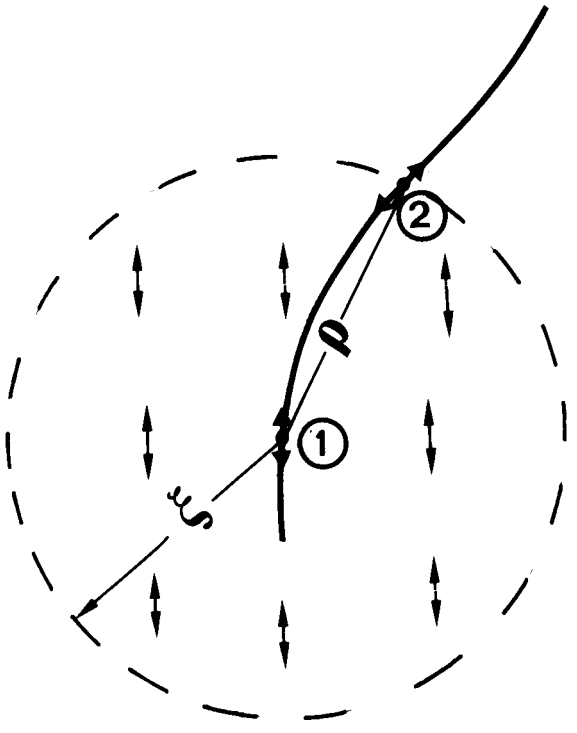

FIGURE 2. Origin of the indirect interactions : a monomer (1) aligns the isotropic medium, and this alignment reacts on a second monomer (2) of the same chain.

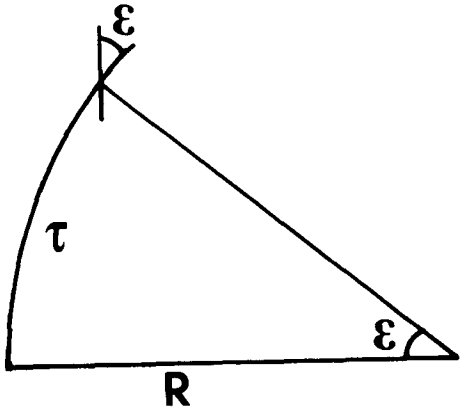

FIGURE 3. Calculation of the stiffness constant B on a bent chain (radius of curvature R).

$$\frac{B}{2R^2} = \int_0^\infty d\tau \, \frac{\Lambda^2}{4\pi L} \, \left(\frac{\tau^2}{R^2}\right) \frac{1}{\tau} \exp(-\tau/\xi) \tag{8}$$

and we reach

$$B = \frac{\Lambda^2}{2\pi L} \xi^2 = \frac{\Lambda^2}{2\pi A} \qquad (l_p > \xi) \tag{9}$$

The rigidity B increases noticeably for $T \to T_c$. Knowing B, a standard calculation gives us the persistence length[10] :

$$l_p = \frac{B}{kT} = \frac{\Lambda^2}{2\pi L k T} \xi^2 \tag{10}$$

Thus $l_p \sim \xi^2/a$ where a is a monomer size, and whenever $\xi/a > 1$ we do expect $l_p > \xi$: in this regime the chains appear as rigid. Similar effects should occur in monomer/polymer solutions (this was pointed out by F. Brochard).

DISCUSSION

1) Upon cooling the melt, the chains should become rigid before reaching $T = T_c$ and this may explain the observed difference in precritical behavior between polymer and monomer.

2) Direct observation on l_p would be most instructive. Various approaches are possible :

Viscosity of the Isotropic Phase

Since the practical materials have rather low degrees of polymerization ($\lesssim 50$), their isotropic melts can probably be described in terms of the Rouse model[11]. Then the viscosity η should be of the form

$$\eta = \eta_0(T) \, R_0^2/a^2 \tag{11}$$

where η_0 is independent of molecular weight, and $R_0 = (2L_0 l_p)^{1/2}$ is the r.m.s. end-to-end radius, L_0 being the extended length. Inserting Eqs. (9), (10) into (11) we get a

significant increase of η near T_c, described by

$$\eta \sim \eta_0(T)\xi^2(T)\ L_0/a^3 \qquad (12)$$

Cis-Trans Fractions in the Spacer

This could possibly be measured by Raman (or IR) spectroscopy, and would give a certain measure of the chain stiffness.

Neutron Diffraction on an isotropic mixtures of H/D chains would measure the gyration radius, which in turn is proportional to R_0.

3) LIMITATIONS

a) Anisotropy of the correlation length

The structure of the gradient terms in Eq. (3) was oversimplified.

b) Self Consistency

Since the chain rigidity will react on the isotropic/nematic phase transition, the Landau parameter A(T) may become dependent on l_p. Related self consistency problems were discussed long ago-in the ordered phase-for molecules undergoing a helix-coil transformation (variable l_p)[12].

The limitations (a) and (b) should be removed simultaneously, and will involve rather heavy numerical work. But the general idea of chain stiffening for $T \to T_c$ in the isotropic phase is probably valid independently of these complications.

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